

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-100308

(43)Date of publication of application : 04.04.2003

(51)Int.Cl.

H01M 4/90
B01J 23/63
B01J 23/652
H01M 4/88
// H01M 8/10

(21)Application number : 2001-288050 (71)Applicant : MITSUBISHI HEAVY IND LTD

(22)Date of filing : 21.09.2001 (72)Inventor : WATANABE SATORU
YASUTAKE SATONOB
NOJIMA SHIGERU

(54) CATHODE ELECTRODE CATALYST FOR FUEL CELL AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cathode electrode catalyst for a fuel cell and the method of manufacturing the same, which can allow the speed of reduction reaction of oxygen in the cathode to increase.

SOLUTION: At least one selected from a group comprising of Sb₂O₄ and CeO₂ is carried to a carrier carrying Pt or Pt-Mo alloy.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against

examiner's decision of rejection]

[Date of extinction of right]

*** NOTICES ***

JPO and NCIPPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The cathode electrode catalyst for fuel cells characterized by making the support which supported the Pt-Mo alloy support at least 1 chosen from the group who consists of Sb₂O₄ and CeO₂, and growing into it.

[Claim 2] The cathode electrode catalyst for fuel cells characterized by making the support which supported Pt support CeO₂, and growing into it.

[Claim 3] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which sinks into a cerium solution, calcinates Pt-Mo alloy support support at 150-200 degrees C in air, and consists of Pt-Mo alloy-CeO₂ support support.

[Claim 4] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which sinks Pt support support into a cerium solution, calcinates this Pt support support at 150-200 degrees C in air, and consists of Pt-CeO₂ support support.

[Claim 5] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which consists of Pt-Mo alloy-CeO₂ support support or Pt-CeO₂ support support by mixing mechanically Pt-Mo alloy support support or Pt support support with the shape 2 of a particle CeO.

[Claim 6] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which calcinates 2OSb₃ powder in air above 500 degrees C, is mixed with Pt-Mo alloy support support on a machine target, and consists of Pt-Mo alloy-Sb₂O₄ support support.

[Translation done.]

*** NOTICES ***

JPO and NCIPPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the cathode electrode catalyst for fuel cells, and its manufacture approach.

[0002]

[Description of the Prior Art] The fuel cell has acquired electromotive force by the cell reaction which obtains water from hydrogen and oxygen. The hydrogen of a raw material makes a original fuel and water, such as a methanol, react to the bottom of existence of a reforming catalyst, and is obtained. It is observed as what can demonstrate the engine performance in which the polymer electrolyte fuel cell (PEFC:Polymer Electrolyte Fuel Cell) was excellent especially among such fuel cells. That is, in the polymer electrolyte fuel cell, hydrogen was used as the fuel and electromotive force has been acquired according to the electrode reaction in an anode (fuel electrode) and a cathode (air pole). The reduction reaction of oxygen has occurred with the cathode here. However, it is surmised that this reduction reaction is slow and constitutes the rate-determining step of electrode reaction. The platinum catalyst is used for the electrode reaction in this cathode in many cases. To improve the catalyst engine performance of this platinum catalyst was desired. This was the same at other fuel cells, such as a phosphoric-acid mold (PAFC) fuel cell.

[0003]

[Problem(s) to be Solved by the Invention] This invention was made to the above-mentioned situation, and aims at offering the cathode electrode catalyst for fuel cells it was made to raise the rate of the reduction reaction of the oxygen in a cathode, and its manufacture approach.

[0004]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the cathode electrode catalyst for fuel cells concerning this invention is characterized by making the support which supported the Pt-Mo alloy support at least 1 chosen from the group who consists of Sb₂O₄ and CeO₂, and growing into it. This invention is a cathode electrode catalyst for fuel cells, and contains what supported CeO₂ in the support which supported Pt as the one gestalt.

[0005] This invention is the manufacture approach of the cathode electrode catalyst for fuel cells as another side face, it sinks into a cerium solution, calcinates Pt-Mo alloy support support at 150-200 degrees C in air, and is characterized by acquiring the cathode electrode catalyst for fuel cells which consists of Pt-Mo alloy-CeO₂ support support.

[0006] Moreover, the manufacture approach of the cathode electrode catalyst for fuel cells concerning this invention sinks Pt support support into a cerium solution, calcinates this Pt support support at 150-200 degrees C in air, and can carry it out also as a gestalt which acquired the cathode electrode catalyst for fuel cells which consists of Pt-CeO₂ support support. Pt-Mo alloy-CeO₂ support support or Pt-CeO₂ support support is obtained also by mixing mechanically Pt-Mo alloy support support or Pt support support with the shape 2 of a particle CeO.

[0007] Furthermore, the manufacture approach of the cathode electrode catalyst for fuel cells concerning this invention is another gestalt, and 2OSb₃ powder is calcinated in air above 500 degrees C, and he mixes with Pt-Mo alloy support support on a machine target, and is trying to obtain Pt-Mo alloy-Sb₂O₄ support support. Although this invention is suitable for a polymer electrolyte fuel cell, otherwise, it is also applicable to fuel cells, such as a phosphoric acid fuel cell.

[0008]

[Embodiment of the Invention] Hereafter, the cathode electrode catalyst for fuel cells concerning this invention and its manufacture approach are further explained to a detail about the gestalt of the operation etc.

[0009] In the fuel cell, it has the platinum catalyst layer by the side of a fuel electrode, and the platinum catalyst layer by the side of an air pole on both sides of the solid-state poly membrane as a gestalt of the 1 operation. Here, the following reactions are performed in an anode (fuel electrode) and a cathode (air pole).

[0010] The following reactions are made to cause by the platinum catalyst layer in an anode.

$H_2 \rightarrow 2H^{++} + 2e^-$ - H^+ produced by this reaction is spread. On the other hand, the following reactions are made to cause by the platinum catalyst layer in a cathode.

$2H^{++} + 2e^- + 1/2O_2 \rightarrow H_2O$ -- these reactions are doubled, a cell reaction is constituted and electromotive force can be acquired.

[0011] Here, as described above, resistance of the reduction reaction of the air by the side of a cathode is considered to constitute the rate-determining step greatly. This invention found out that such resistance decreased sharply by using the co-catalyst of at least 1 chosen from the group who consists of Sb_2O_4 and CeO_2 further, as a result of examining wholeheartedly the electrode catalyst using the Pt-Mo alloy used for a platinum catalyst layer. Although not completely supported about the principle, it is thought that it calls at the place mostly explained below about drawing 1. As shown in drawing 1, the oxygen molecule 3 is first captured by the co-catalyst particle 2 on the support particle 1. This oxygen molecule 3 is lengthened by Mo component in the particle 4 of a Pt-Mo alloy, and carries out spillover to the Pt-Mo alloy particle 4. The catalyst property of Pt component is demonstrated by this and the reduction reaction of oxygen advances promptly by it. In addition, when making Sb_2O_4 into a co-catalyst, this invention persons will check the effectiveness of resistance reduction only by supporting to the ability not checking effectiveness on the support which supported only Pt with CeO_2 , if they are not Pt-Mo alloys. Therefore, like the mechanism of drawing 1, when CeO_2 is used, it is guessed that the spillover of oxygen is what advances even if there is no Mo.

[0012] The powder of said support has desirable carbon powder, for example, a graphite, carbon black, the activated carbon that has electric conductivity can be mentioned. Especially, for the electrode catalyst for fuel cells, KETCHIEN carbon and Balkan Peninsula carbon are desirable.

[0013] As for the ratio of the Pt-Mo alloy in Pt-Mo alloy support carbon when a Pt-Mo alloy is used and the ratio of Mo in the Pt-Mo alloy content contained in the cathode electrode catalyst for fuel cells supports a 1-99-mol % and Pt-Mo alloy to carbon, it is desirable that it is 1 - 99wt%. Moreover, when using a Pt-Mo alloy, the amount of support of CeO_2 and Sb_2O_4 as a co-catalyst has 0.01 to 10 desirable times to the weight of Pt-Mo alloy support carbon.

[0014] When using not a Pt-Mo alloy but Pt, as for the ratio of Pt in Pt support carbon at the time of supporting Pt to carbon, it is desirable that it is 1 - 99wt%. Moreover, when using Pt, the amount of support of CeO_2 and Sb_2O_4 as a co-catalyst has 0.01 to 10 desirable times to the weight of Pt support carbon.

[0015] Subsequently, about the manufacture approach of the cathode electrode catalyst for fuel cells concerning this invention, the case where a catalytic activity component is supported is mentioned to carbon support, and the gestalt of the operation is explained.

[0016] Pt solution is prepared so that the molar quantity of Pt may turn into a predetermined amount. As a Pt solution, H_2PtCl_6 solution and Pt complex ion solution of $Pt(NO_2)_2(NH_3)_2$ grade can be mentioned. It mixes in the water / ethanol mixed solution which boiled this Pt solution, and Pt ion is returned. Carbon powder, such as KETCHIEN carbon used as the carbon support after cooling, is added, and carbon powder is made to carry out adsorption support of the Pt. Then, it filters and dries, and heat-treats in a hydrogen ambient atmosphere, and Pt support carbon is obtained.

[0017] Next, it sinks into molybdenum water solutions, such as 5 molybdenum chloride water solutions 0.1 to 2 twice the amount of Mo of the number of mols of Pt, Pt support carbon is returned to them at 250 degrees C - 800 degrees C by hydrogen, and Pt-Mo alloy support carbon is obtained. Next, it sinks into PtMo support carbon and cerium water solutions, such as a cerium-nitrate water solution, are calcinated at 150-200 degrees C among air so that 0.01 to 10 times as many CeO_2 as

this may be included to the weight of Pt, and Pt-Mo alloy-CeO₂ support carbon is obtained.

[0018] If it sinks into Pt support carbon and cerium water solutions, such as a cerium-nitrate water solution, are calcinated at 150-200 degrees C in air so that 0.01 to 10 times as many CeO₂ as this may be included to the weight of Pt above, without supporting Mo, Pt-CeO₂ support carbon can be obtained.

[0019] Moreover, instead of CeO₂ after obtaining Pt-Mo alloy support carbon, Sb₂O₄ is made to support and it is a Pt-Mo alloy. - Sb₂O₄ Support carbon can be obtained. In this case, 2OSb₃ powder (particle size of 0.1 micrometers or less) can be calcinated in air above 500 degrees C so that it may be set to 0.01 to 10 times as much Sb₂O₄ as the weight of Pt-Mo alloy support carbon, and it can mix with Pt-Mo alloy support carbon on a machine target, and Pt-Mo alloy-Sb₂O₄ support carbon can be obtained. If it carries out to baking and coincidence of Sb₂O₄ in 500 degrees C or more, it will mix for a carbon component burning out mechanically.

[0020] In addition, a commercial item can also be used for Pt support carbon (Pt/C) and Pt-Mo alloy support carbon (PtMo/C) as it is. It can mix mechanically to Pt-Mo alloy support carbon, and Pt-Mo alloy-CeO₂ support carbon can also acquire the shape 2 of a particle CeO to it.

[0021]

[Example] H₂PtCl₆ solution (Pt content of 100g/l.) was diluted to 1g metal / l so that the molar quantity of example 1Pt might be set to 0.6mmol(s). The solution (1440g [of ion exchange water] and ethanol 1140g and polyvinyl alcohol 0.4g) was boiled. This boiling solution was made to add and carry out the reaction of the Pt ion solution prepared previously for 15 minutes (usually 10 minutes - 24 hours), and Pt ion was returned to it. 120mg (KETCHIEN carbon whose specific surface area is 800m²/g) of carbon powder was added and stirred after cooling, and carbon was made to carry out adsorption support of the Pt. Then, it filtered and dried, and in the hydrogen ambient atmosphere, heat treatment was carried out for 1 hour (usually 0.5 - 6 hours), pyrolysis removal of the polyvinyl alcohol was carried out, and 250 degrees C of Pt support carbon catalysts were acquired. Next, it sank into 5 molybdenum chloride water solutions 1 time (usually 0.1 to 2 twice) the amount of Mo of the number of mols of Pt, Pt support carbon was returned to them by hydrogen at 500 degrees C (usually 250 degrees C - 800 degrees C), and Pt-Mo alloy support carbon was obtained. Next, it sank into Pt-Mo alloy support carbon, the cerium-nitrate water solution was calcinated at 200 degrees C among air, and Pt-Mo alloy-CeO₂ support carbon was obtained.

[0022] H₂PtCl₆ solution (Pt content of 100g/l.) was diluted to 1g metal / l so that the molar quantity of example 2Pt might be set to 0.6mmol(s). The solution (1440g [of ion exchange water] and ethanol 1140g and polyvinyl alcohol 0.4g) was boiled. This boiling solution was made to add and carry out the reaction of the Pt ion solution prepared previously for 15 minutes (usually 10 minutes - 24 hours), and Pt ion was returned to it. 120mg (KETCHIEN carbon whose specific surface area is 800m²/g) of carbon powder was added and stirred after cooling, and carbon was made to carry out adsorption support of the Pt. Then, it filtered and dried, and in the hydrogen ambient atmosphere, heat treatment was carried out for 1 hour (usually 0.5 - 6 hours), pyrolysis removal of the polyvinyl alcohol was carried out, and 250 degrees C of Pt support carbon catalysts were acquired. Next, it sank into Pt support carbon and the cerium-nitrate water solution was calcinated at 200 degrees C among air so that twice (usually 0.01 to 10 times) as many CeO₂ as this might be included to the weight of Pt, and Pt-CeO₂ support carbon was obtained.

[0023] H₂PtCl₆ solution (Pt content of 100g/l.) was diluted to 1g metal / l so that the molar quantity of example 3Pt might be set to 0.6mmol(s). The solution (1440g [of ion exchange water] and ethanol 1140g and polyvinyl alcohol 0.4g) was boiled. This boiling solution was made to add and carry out the reaction of the Pt ion solution prepared previously for 15 minutes (usually 10 minutes - 24 hours), and Pt ion was returned to it. 120mg (KETCHIEN carbon whose specific surface area is 800m²/g) of carbon powder was added and stirred after cooling, and carbon was made to carry out adsorption support of the Pt. Then, it filtered and dried, and in the hydrogen ambient atmosphere, heat treatment was carried out for 1 hour (usually 0.5 - 6 hours), pyrolysis removal of the polyvinyl alcohol was carried out, and 250 degrees C of Pt support carbon catalysts were acquired. Next, it sank into 5 molybdenum chloride water solutions 1 time (usually 0.1 to 2 twice) the amount of Mo of the number of mols of Pt, Pt support carbon was returned to them at 250 degrees C - 800 degrees C by hydrogen, and Pt-Mo alloy support carbon was obtained. Next, 2OSb₃ powder (particle size of

0.1 micrometers or less) was calcinated in air above 500 degrees C so that it might be set to twice (usually 0.01 to 10 times) as many Sb 2O4 as the weight of Pt-Mo alloy support carbon, and it mixed with Pt-Mo alloy support carbon on the machine target, and Pt-Mo alloy-Sb2O4 support carbon was obtained.

[0024] The polymer electrolyte fuel cell was manufactured using the cathode electrode catalyst of example 4 examples 1-3, the trial was performed, and the generation-of-electrical-energy engine performance was evaluated.

[0025] (Preparation of a cell cel) The Nafion solution was added as a polyelectrolyte solution for the anode electrode catalyst (PtRu alloy support carbon) at water / ethanol mixed liquor list, and the slurry was prepared by ultrasonic stirring. The obtained slurry was applied to the Teflon (trademark) sheet, it imprinted on one side of the solid-state poly membrane (at the Du Pont make, a trade name is the Nafion film) of 50 micrometers of thickness, and the anode pole was formed. The amount of Pt (s) in an anode pole was 0.5 mg/cm², the amount of Ru was 0.5 mg/cm², and the amount of Nafion was 1 mg/cm².

[0026] On the other hand, the Nafion solution was added as a polyelectrolyte solution for the cathode electrode catalyst of examples 1-3 at water / ethanol mixed liquor list, and the slurry was prepared by ultrasonic stirring. It imprinted to the field which applied the obtained slurry to the Teflon sheet and imprinted the anode of the solid-state poly membrane (a trade name is the Nafion film at the Du Pont make) of 50 micrometers of thickness, and the field of the opposite side, and the cathode pole was formed. The amount of Pt(s) in a cathode pole was 0.5 mg/cm², and the amount of Nafion was 0.5 mg/cm². After sticking carbon paper on an anode pole and each cathode pole, these were inserted with one pair of separators, and the electrode cel of 5cm around was produced.

[0027] <Generation-of-electrical-energy performance evaluation> About the obtained electrode cels 1-3, a generation-of-electrical-energy trial is performed by the test condition explained below, and the result is shown in the following table 1.

[0028] anode side: -- an H₂ 60%, CO₂ 20%, and N₂ 20% side and a ppm, 2ata, temperature [of 80 degrees C], and 80% cathode [of CO10 hydrogen utilization factors] side -- :air (Air), 2ata, the temperature of 80 degrees C, and 40% [Table 1] of air utilization rates

	0.15A/cm ²	0.35A/cm ²	0.7A/cm ²
電極 1	0.80 V	0.76 V	0.65 V
電極 2	0.80 V	0.76 V	0.65 V
電極 3	0.82 V	0.76 V	0.66 V
従来電極	0.78 V	0.70 V	0.60 V

[0029] Compared with a cel, it turns out conventionally that the electrode cels 1-3 using the prototype catalysts 1-3 are highly efficient so that clearly from Table 1. In addition, the above-mentioned example followed the polymer electrolyte fuel cell. However, this invention is not limited to such a thing and can be applied to other fuel cells, such as a phosphoric acid fuel cell.

[0030]

[Effect of the Invention] According to this invention, the cathode electrode catalyst for fuel cells it was made to raise the rate of the reduction reaction of the oxygen in a cathode, and its manufacture approach are offered so that clearly from the above-mentioned place.

[Translation done.]

*** NOTICES ***

JPO and NCIPPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a conceptual diagram explaining the mechanism of reduction of the oxygen in this invention.

[Description of Notations]

- 1 Support Particle
- 2 Co-catalyst Particle
- 3 Oxygen Molecule
- 4 Alloy Particle

[Translation done.]

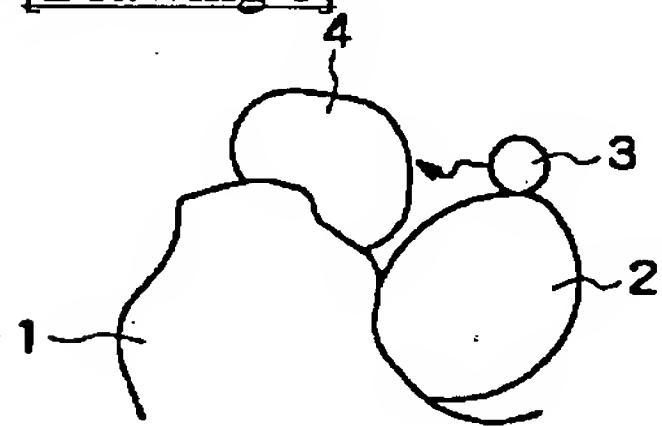
*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-100308
(43)Date of publication of application : 04.04.2003

(51)Int.CI. H01M 4/90
B01J 23/63
B01J 23/652
H01M 4/88
// H01M 8/10

(21)Application number : 2001-288050 (71)Applicant : MITSUBISHI HEAVY IND LTD
(22)Date of filing : 21.09.2001 (72)Inventor : WATANABE SATORU
YASUTAKE SATONOBU
NOJIMA SHIGERU

**(54) CATHODE ELECTRODE CATALYST FOR FUEL CELL AND METHOD OF
MANUFACTURING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cathode electrode catalyst for a fuel cell and the method of manufacturing the same, which can allow the speed of reduction reaction of oxygen in the cathode to increase.

SOLUTION: At least one selected from a group comprising of Sb₂O₄ and CeO₂ is carried to a carrier carrying Pt or Pt-Mo alloy.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of
rejection]

[Kind of final disposal of application other than
the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2003-100308

(P2003-100308A)

(43)公開日 平成15年4月4日(2003.4.4)

(51)Int.Cl. ⁷	識別記号	F I	データード*(参考)
H 01 M 4/90		H 01 M 4/90	B 4 G 0 6 9
B 01 J 23/63		4/88	K 5 H 0 1 8
23/652		8/10	5 H 0 2 6
H 01 M 4/88		B 01 J 23/64	1 0 3 M
// H 01 M 8/10		23/56	3 0 1 M

審査請求 未請求 請求項の数 6 OL (全 5 頁)

(21)出願番号 特願2001-288050(P2001-288050)

(71)出願人 000006208

三菱重工業株式会社

東京都千代田区丸の内二丁目5番1号

(22)出願日 平成13年9月21日(2001.9.21)

(72)発明者 渡辺 哲

広島県広島市西区観音新町四丁目6番22号

三菱重工業株式会社広島研究所内

(72)発明者 安武 聰信

広島県広島市西区観音新町四丁目6番22号

三菱重工業株式会社広島研究所内

(74)代理人 100099623

弁理士 奥山 尚一 (外2名)

最終頁に続く

(54)【発明の名称】 燃料電池用カソード電極触媒およびその製造方法

(57)【要約】

【課題】 カソードにおける酸素の還元反応の速度を上昇させるようにした燃料電池用カソード電極触媒およびその製造方法を提供する。

【解決手段】 PtまたはPt-Mo合金を担持した担体に、Sb₂O₃とCeO₂から成るグループから選択した少なくとも一を担持させた。

【特許請求の範囲】

【請求項1】 Pt-Mo合金を担持した担体に、Sb₂O₃とCeO₂から成るグループから選択した少なくとも一を担持させて成ることを特徴とする燃料電池用カソード電極触媒。

【請求項2】 Ptを担持した担体に、CeO₂を担持させて成ることを特徴とする燃料電池用カソード電極触媒。

【請求項3】 Pt-Mo合金担持担体をセリウム溶液に含浸し、空気中で150～200℃で焼成し、Pt-Mo合金-CeO₂担持担体から成る燃料電池用カソード電極触媒を得ることを特徴とする燃料電池用カソード電極触媒の製造方法。

【請求項4】 Pt担持担体をセリウム溶液に含浸し、該Pt担持担体を空気中で150～200℃で焼成し、Pt-CeO₂担持担体から成る燃料電池用カソード電極触媒を得るようにしたことを特徴とする燃料電池用カソード電極触媒の製造方法。

【請求項5】 Pt-Mo合金担持担体またはPt担持担体を微粒子状CeO₂と機械的に混合することによって、Pt-Mo合金-CeO₂担持担体またはPt-CeO₂担持担体から成る燃料電池用カソード電極触媒を得ることを特徴とする燃料電池用カソード電極触媒の製造方法。

【請求項6】 Sb₂O₃粉末を500℃以上で空気中で焼成し、Pt-Mo合金担持担体と機械的に混合し、Pt-Mo合金-Sb₂O₃担持担体から成る燃料電池用カソード電極触媒を得ることを特徴とする燃料電池用カソード電極触媒の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、燃料電池用カソード電極触媒およびその製造方法に関するものである。

【0002】

【従来の技術】燃料電池は、水素と酸素から水を得る電池反応によって起電力を得ている。原料の水素は、メタノールなどの原燃料と水を改質触媒の存在下に反応させて得られる。このような燃料電池のうち、特に、固体高分子型燃料電池(PEFC: Polymer Electrolyte Fuel Cell)が優れた性能を発揮できるものとして注目されている。すなわち、固体高分子型燃料電池では、水素を燃料とし、アノード(燃料極)、カソード(空気極)における電極反応によって起電力を得ている。ここでカソードでは、酸素の還元反応が起こっている。しかし、この還元反応が遅く、電極反応の律速段階を構成していると推測される。このカソードにおける電極反応には、白金触媒が用いられていることが多い。かかる白金触媒の触媒性能を上げることが望まれていた。このことは、リン酸型(PAFC)燃料電池等の他の燃料電池でも同様であった。

10

【0003】

【発明が解決しようとする課題】本発明は上記事情に対してなされたもので、カソードにおける酸素の還元反応の速度を上昇させるようにした燃料電池用カソード電極触媒およびその製造方法を提供することを目的とする。

【0004】

【課題を解決するための手段】上記目的を達成するため、本発明に係る燃料電池用カソード電極触媒は、Pt-Mo合金を担持した担体に、Sb₂O₃とCeO₂から成るグループから選択した少なくとも一を担持させて成ることを特徴とする。本発明は、燃料電池用カソード電極触媒であって、Ptを担持した担体に、CeO₂を担持したものもその一形態として含む。

【0005】本発明は、別の側面として燃料電池用カソード電極触媒の製造方法であり、Pt-Mo合金担持担体をセリウム溶液に含浸し、空気中で150～200℃で焼成し、Pt-Mo合金-CeO₂担持担体から成る燃料電池用カソード電極触媒を得ることを特徴とする。

【0006】また、本発明に係る燃料電池用カソード電極触媒の製造方法は、Pt担持担体をセリウム溶液に含浸し、該Pt担持担体を空気中で150～200℃で焼成し、Pt-CeO₂担持担体から成る燃料電池用カソード電極触媒を得るようにした形態としても実施できる。Pt-Mo合金-CeO₂担持担体またはPt-CeO₂担持担体は、Pt-Mo合金担持担体またはPt担持担体を微粒子状CeO₂と機械的に混合することによっても得られる。

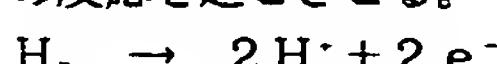
【0007】さらに、本発明に係る燃料電池用カソード電極触媒の製造方法は、別の形態で、Sb₂O₃粉末を500℃以上で空気中で焼成し、Pt-Mo合金担持担体と機械的に混合し、Pt-Mo合金-Sb₂O₃担持担体を得るようにしている。本発明は、固体高分子型燃料電池に好適であるが、他にも、リン酸型燃料電池等の燃料電池に適用することもできる。

【0008】

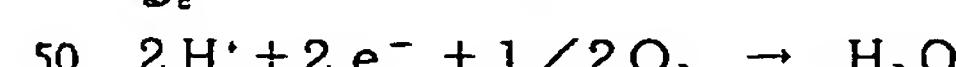
【発明の実施の形態】以下、本発明に係る燃料電池用カソード電極触媒およびその製造方法をその実施の形態等についてさらに詳細に説明する。

【0009】燃料電池では、その一実施の形態として、固体高分子膜を挟んで燃料極側の白金触媒層と、空気極側の白金触媒層とを備えている。ここで、アノード(燃料極)、カソード(空気極)では、下記のような反応が行われる。

【0010】アノードにおいて白金触媒層により、以下の反応を起こさせる。



この反応によって生じるH⁺が拡散する。一方、カソードにおいて白金触媒層により、以下の反応を起こさせる。



これらの反応を合わせて電池反応が構成され、起電力を得ることができる。

【0011】ここで、前記したように、カソード側の空気の還元反応の抵抗が大きく律速段階を構成しているものと思われる。本発明者は、白金触媒層に用いるPt-Mo合金を用いた電極触媒について、鋭意検討した結果、さらにSb₂O₃とCeO₂から成るグループから選択した少なくとも一の助触媒を用いることによって、このような抵抗が大幅に減少することを見出した。その原理については、完全には裏付けられていないものの、ほぼ図1について以下に説明するところによると思われる。図1に示すように、まず、担体粒子1上の助触媒粒子2に酸素分子3が捕獲される。該酸素分子3は、Pt-Mo合金の粒子4中のMo成分に引かれてPt-Mo合金粒子4にスピルオーバーする。これによって、Pt成分の触媒特性が発揮され、酸素の還元反応が速やかに進行する。なお、本発明者らは、Sb₂O₃を助触媒とする場合には、Pt-Mo合金でなければ効果が確認できないのに対し、CeO₂で単にPtだけを担持した担体上に担持するだけで抵抗低減の効果を確認している。したがって、図1のメカニズムのように酸素のスピルオーバーは、CeO₂を用いた場合、Moがなくても進行するものと推測される。

【0012】前記担体の粉末は、炭素粉末が好ましく、例えば、黒鉛、カーボンブラック、電気導電性を有する活性炭等を挙げることができる。特に、燃料電池用電極触媒には、ケッテンカーボン、バルカンカーボンが好ましい。

【0013】Pt-Mo合金を用いる場合、燃料電池用カソード電極触媒に含まれるPt-Mo合金成分中のMoの比率は1～99モル%、Pt-Mo合金をカーボンに担持した場合のPt-Mo合金担持カーボン中のPt-Mo合金の比率は、1～99wt%であることが好ましい。また、Pt-Mo合金を用いる場合、助触媒としてのCeO₂、Sb₂O₃の担持量は、Pt-Mo合金担持カーボンの重量に対し、0.01～10倍が好ましい。

【0014】Pt-Mo合金ではなく、Ptを用いる場合、Ptをカーボンに担持した場合のPt担持カーボン中のPtの比率は、1～99wt%であることが好ましい。また、Ptを用いる場合、助触媒としてのCeO₂、Sb₂O₃の担持量は、Pt担持カーボンの重量に対し、0.01～10倍が好ましい。

【0015】次いで、本発明に係る燃料電池用カソード電極触媒の製造方法について、カーボン担体に触媒活性成分を担持する場合を挙げてその実施の形態を説明する。

【0016】Ptのモル量が所定の量になるようにPt溶液を調製する。Pt溶液としては、H₂PtCl₆溶液、Pt(NO₃)₄、(NH₄)₂等のPt錯イオン溶液を

挙げることができる。このPt溶液を沸騰した水/エタノール混合溶液中に混合し、Ptイオンを還元する。冷却後カーボン担体となるケッテンカーボン等のカーボン粉末を添加し、カーボン粉末にPtを吸着担持させる。その後、ろ過、乾燥し、水素雰囲気中で熱処理し、Pt担持カーボンを得る。

【0017】次に、Ptのモル数の0.1～2倍のMo量の5塩化モリブデン水溶液等のモリブデン水溶液にPt担持カーボンを含浸し、水素で250℃～800℃で還元し、Pt-Mo合金担持カーボンを得る。次に、Ptの重量に対して0.01～10倍のCeO₂を含むように硝酸セリウム水溶液等のセリウム水溶液をPtMo担持カーボンに含浸し、空気中150～200℃で焼成し、Pt-Mo合金-CeO₂担持カーボンを得る。

【0018】以上で、Moを担持せずに、Ptの重量に対して0.01～10倍のCeO₂を含むように硝酸セリウム水溶液等のセリウム水溶液をPt担持カーボンに含浸し、空気中で150～200℃で焼成すれば、Pt-CeO₂担持カーボンを得ることができる。

【0019】また、Pt-Mo合金担持カーボンを得た後、CeO₂の代わりに、Sb₂O₃を担持させて、Pt-Mo合金-Sb₂O₃担持カーボンを得ることができる。この場合、Pt-Mo合金担持カーボンの重量の0.01～10倍のSb₂O₃となるようにSb₂O₃粉末(粒径0.1μm以下)を500℃以上で空気中で焼成し、Pt-Mo合金担持カーボンと機械的に混合し、Pt-Mo合金-Sb₂O₃担持カーボンを得ることができ。機械的に混合するには、500℃以上におけるSb₂O₃の焼成と同時に行うと、カーボン成分が燃えてしまうためである。

【0020】なお、Pt担持カーボン(Pt/C)、Pt-Mo合金担持カーボン(PtMo/C)は、市販品をそのまま用いることもできる。Pt-Mo合金-CeO₂担持カーボンはPt-Mo合金担持カーボンに微粒子状CeO₂を機械的に混合して得ることもできる。

【0021】

【実施例】実施例1

Ptのモル量が0.6mmolになるようにH₂PtCl₆溶液(Pt含有量100g/1)を1g金属/1に希釈した。イオン交換水1440g、エタノール1140g、ポリビニルアルコール0.4gの溶液を沸騰させた。この沸騰した溶液に、先に調製したPtイオン溶液を添加し、15分(通常、10分～24時間)反応させ、Ptイオンを還元した。冷却後、カーボン粉末(比表面積が800m²/gのケッテンカーボン)120mgを添加、攪拌し、カーボンにPtを吸着担持させた。その後、ろ過、乾燥し、水素雰囲気中で250℃、1時間(通常、0.5～6時間)熱処理し、ポリビニルアルコールを熱分解除去し、Pt担持カーボン触媒を得た。次に、Ptのモル数の1倍(通常、0.1～2倍)

のMo量の5塩化モリブデン水溶液にPt担持カーボンを含浸し、水素で500°C(通常、250°C~800°C)で還元し、Pt-Mo合金担持カーボンを得た。次に、硝酸セリウム水溶液をPt-Mo合金担持カーボンに含浸し、空気中200°Cで焼成し、Pt-Mo合金-CeO₂担持カーボンを得た。

【0022】実施例2

Ptのモル量が0.6mmolになるようにH₂PtC₁₆溶液(Pt含有量100g/1)を1g金属/1に希釈した。イオン交換水1440g、エタノール1140g、ポリビニルアルコール0.4gの溶液を沸騰させた。この沸騰した溶液に、先に調製したPtイオン溶液を添加し、15分(通常、10分~24時間)反応させ、Ptイオンを還元した。冷却後、カーボン粉末(比表面積が800m²/gのケッテンカーボン)120mgを添加、攪拌し、カーボンにPtを吸着担持させた。その後、ろ過、乾燥し、水素雰囲気中で250°C、1時間(通常、0.5~6時間)熱処理し、ポリビニルアルコールを熱分解除去し、Pt担持カーボン触媒を得た。次に、Ptの重量に対して2倍(通常、0.01~10倍)のCeO₂を含むように硝酸セリウム水溶液をPt担持カーボンに含浸し、空気中200°Cで焼成し、Pt-CeO₂担持カーボンを得た。

【0023】実施例3

Ptのモル量が0.6mmolになるようにH₂PtC₁₆溶液(Pt含有量100g/1)を1g金属/1に希釈した。イオン交換水1440g、エタノール1140g、ポリビニルアルコール0.4gの溶液を沸騰させた。この沸騰した溶液に、先に調製したPtイオン溶液を添加し、15分(通常、10分~24時間)反応させ、Ptイオンを還元した。冷却後、カーボン粉末(比表面積が800m²/gのケッテンカーボン)120mgを添加、攪拌し、カーボンにPtを吸着担持させた。その後、ろ過、乾燥し、水素雰囲気中で250°C、1時間(通常、0.5~6時間)熱処理し、ポリビニルアルコールを熱分解除去し、Pt担持カーボン触媒を得た。次に、Ptのモル数の1倍(通常、0.1~2倍)のMo量の5塩化モリブデン水溶液にPt担持カーボンを含浸し、水素で250°C~800°Cで還元し、Pt-Mo合金担持カーボンを得た。次に、Pt-Mo合金担持カーボンの重量の2倍(通常、0.01~10倍)のSb₂O₃となるようにSb₂O₃粉末(粒径0.1μm以下)を500°C以上で空気中で焼成し、Pt-Mo合金担持カーボンと機械的に混合し、Pt-Mo合金-Sb₂O₃担持カーボンを得た。

【0024】実施例4

実施例1~3のカソード電極触媒を用いて固体高分子型燃料電池を製造し、その試験を行い、発電性能を評価した。

【0025】(電池セルの調製)アノード電極触媒(Pt

Ru合金担持カーボン)に水/エタノール混合液並びに高分子電解質溶液としてナフィオン溶液を添加して超音波攪拌にてスラリーを調製した。得られたスラリーをテフロン(登録商標)シートに塗布して膜厚50μmの固体高分子膜(デュポン社製で、商品名がナフィオン膜)の片面に転写し、アノード極を形成した。アノード極中のPt量は0.5mg/cm²で、Ru量は0.5mg/cm²で、ナフィオン量は1mg/cm²であった。

10 【0026】一方、実施例1~3のカソード電極触媒に水/エタノール混合液並びに高分子電解質溶液としてナフィオン溶液を添加して超音波攪拌にてスラリーを調製した。得られたスラリーをテフロンシートに塗布して膜厚50μmの固体高分子膜(デュポン社製で、商品名がナフィオン膜)のアノードを転写した面と反対側の面に転写し、カソード極を形成した。カソード極中のPt量は0.5mg/cm²で、ナフィオン量は0.5mg/cm²であった。アノード極及びカソード極それぞれにカーボンペーパーを貼り付けた後、これらを1対のセパレータで挟み、5cm四方の電極セルを作製した。

【0027】<発電性能評価>得られた電極セル1~3について、下記に説明する試験条件で発電試験を行い、その結果を下記表1に示す。

【0028】アノード側: H₂ 60%、CO₂ 20%、N₂ 20%、CO 10ppm、2ata、温度80°C、水素利用率80%

カソード側: 空気(Air)、2ata、温度80°C、空気利用率40%

【表1】

	0.15A/cm ²	0.35A/cm ²	0.7A/cm ²
電極1	0.80 V	0.76 V	0.66 V
電極2	0.80 V	0.76 V	0.66 V
電極3	0.82 V	0.76 V	0.66 V
従来電極	0.78 V	0.70 V	0.60 V

【0029】表1から明らかなように、試作触媒1~3を用いた電極セル1~3は、従来セルに比べ高性能であることがわかる。なお、上記実施例は、固体高分子型燃料電池について行った。しかし、本発明は、このようなものに限定されるものではなく、リン酸型燃料電池等の他の燃料電池にも適用することができる。

【0030】

【発明の効果】上記したところから明らかなように、本発明によれば、カソードにおける酸素の還元反応の速度を上昇させるようにした燃料電池用カソード電極触媒およびその製造方法が提供される。

【図面の簡単な説明】

【図1】本発明における酸素の還元のメカニズムを説明する概念図である。

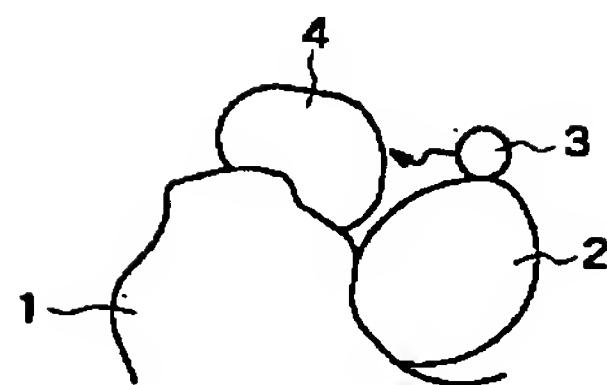
【符号の説明】

1 担体粒子
2 助触媒粒子

* 3
* 4

酸素分子
合金粒子

【図1】



フロントページの続き

(72)発明者 野島 繁

広島県広島市西区観音新町四丁目6番22号
三菱重工業株式会社広島研究所内

F ターム(参考) 4G069 AA03 AA08 BA08A BA08B
BB02A BB02B BB04A BB04B
BC26A BC26B BC43A BC43B
BC59A BC59B BC75A BC75B
CC32 EC04Y FA02 FB07
FB14 FB19 FB30 FC07
5H018 AA06 AS03 BB01 BB05 BB12
EE08 EE10 EE12 HH08
5H026 AA06 BB00 BB01 BB03 BB08
EE08 EE12 HH08